CLINTON LABORATORIES

CENTRAL FILES NUMBER

47-9 538

#1279

Date September 25, 1947

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To G. W. Parker

From S. Freed, G. M. Hebert, J. B. Dial, A. D. Bogard and A. R. Brosi

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#1279

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Preparation of I^{135} for Xe^{135} Cross Section Measurements

I. Introduction

In the work of Borst and co-workers on the cross section of Xe^{135} as a function of neutron energy, fission product iodine was recovered and precipitated with carrier iodine as PdI_2. After growth of the Xe^{135} daughter, the PdI_2 precipitate was used as the absorbing sample in the crystal spectrometer.

Their process for recovery of fission product iodine consisted of dissolving the uranium metal in HCl, oxidizing U^{+4} to UO_2^{+2} with concentrated $Na_2Cr_2O_7$ and distilling off the iodine into a $PdCl_2$ solution saturated with SO_2. PdI_2 precipitated when the SO_2 was removed by boiling.

Very erratic results have been obtained in attempts to repeat this process. The work done in order to get consistently high yields is reported here. Essentially the same process has been used, the most important modification being more precise control of the oxidation step.

II. Experimental

The reaction vessel was a three liter flask with nine standard taper necks. Into these necks were fitted (1) a reflux condenser, (2) a Pt electrode, (3) a saturated KCl salt bridge, (4) a thermocouple well, (5) a tungsten electrode, (6) a stirrer, (7) (8) and (9) capillary tubes for the addition of various oxidizing and reducing solutions. The flask was mounted in a glycerine bath on a hot plate so that iodine could be distilled out.

In order to follow the oxidation reaction the potential of the Pt (U^{+4}, UO_2^{+2}) electrode with a saturated calomel reference electrode was measured using a continuous reading vacuum tube voltmeter which drew 10^{-9} to 10^{-10} amps. In some of the later work, tungsten was used as a reference electrode in order to eliminate use of a salt bridge.

In order to determine iodine yields and study distillation rates, 1 to 2 mc of I^{131} tracer was used. The γ radiation was detected and recorded using a counting rate meter. In different experiments the G-M tube was located in order to determine the change in the amount of iodine (1) in the reaction vessel, (2) in the vapor over the solution, (3) in the reflux condenser, and (4) in the receiving flask.

III. Solution of Uranium Metal

It is proposed to isolate the iodine from six uranium slugs in the

active runs. The process development work was done with one quarter slug (1/24 scale). In the first experiments about three hours were required to dissolve a quarter slug in 550 ccs of concentrated HCl. Later, the metal was suspended in a Pt gauze basket so it could be removed from the solution after one hour. It was found that contact with the Pt gauze increased the rate of solution to such an extent that practically all of the metal was dissolved after one hour. In many of the succeeding experiments all of the metal was dissolved and never did more than 5% remain undissolved after one hour.

Since it was thought that this increase in rate of solution was due to a reduction in overvoltage the Pt basket was platinized. Any increase in the rate of solution caused by this was too small to be readily apparent.

In two experiments the gases from the dissolving reaction were scrubbed with an alkaline sulfite solution. In these cases iodine carrier and tracer were added to the concentrated HCl before the metal was dissolved. Analysis of the scrubbing solution showed that about 10% of the HCl escaped from the condenser but not more than a few tenths of a per cent of iodine was lost.

IV. Oxidation of Uranium and Iodine

In preliminary experiments on the oxidation of iodide ion in boiling UCl_4 solutions with concentrated $Na_2Cr_2O_7$ solutions, iodine yields were found to vary from 10 to 50%. It was found that on reducing with $NH_2OH \cdot HCl$ more iodine was liberated giving a total yield which was seldom more than 60% and in most cases much less.

When potentiometric measurements were made it was found that iodine was evolved only at the U^{+4} end point. Even with dilute dichromate solutions the end point was so sharp that it was impossible to stop addition at the optimum point. When iron was added to catalyze the U^{+4} oxidation it was found that iodine was liberated in the region buffered by the Fe^{+2}, Fe^{+3} couple.

Attempts were then made to measure the relative iodine vapor pressure as a function of oxidation-reduction potential. One milligram of iodine and 2 mc of I^{131} were added to a solution of one-fourth uranium slug in 550 ccs of concentrated HCl. The solution was boiled and counting rates were determined using a shielded tube located between the flask and a reflux condenser. In these crude measurements it appeared that the iodine vapor pressure was a maximum in the region where Fe^{+3}/Fe^{+2} was from 1 to 6. Since iodine was collecting in the reflux condenser during the measurements they were not very reliable. Distillation of iodine was possible in this region but the rates were too slow.

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When $Na_2Cr_2O_7$ was used as oxidant the solubility of NaCl was exceeded. Since the presence of this solid phase might complicate the process it was eliminated by using $Li_2Cr_2O_7$. With $Li_2Cr_2O_7$ as oxidant and a Fe^{+3}/Fe^{+2} ratio of two, yields of 65 to 70% were obtained after one hour of distillation.

Since sulfate ion decreases the solubility of iodine the iron was added as a concentrated $Fe_2(SO_4)_3$ solution in the next experiments. One-third of the iron (25 ccs of a saturated $Fe_2(SO_4)_3$ solution) was added before the $Li_2Cr_2O_7$ and two-thirds (50 ccs) was added after oxidation to the U^{+4} end point.

In the presence of sulfate ion the iodine could be distilled out at a rate proportional to the amount of iodine present until the total iodine was reduced to about 0.25 mg when the rate decreased more rapidly. The time required to distill 50% of the iodine was 4 to 8 minutes. By adding one-half the carrier (0.5 mg) and distilling for 10 minutes, then adding the remaining 0.5 mg and distilling, it was possible to collect 90% of the tracer in thirty minutes.

An attempt was made to oxidize with H_2O_2 rather than $Li_2Cr_2O_7$ in order that the U^{+4} end point could be determined by the color change. At the end point $FeSO_4$ and $Fe_2(SO_4)_3$ were added to give a Fe^{+3}/Fe^{+2} ratio of two. The time required to distill out 50% of the iodine (0.5 mg) was twenty-five minutes. This was considered too slow for a process involving the 6.7 h I^{135}.

In another experiment no carrier iodine was added. The U^{+4} was oxidized with $Li_2Cr_2O_7$ and a Fe^{+3}/Fe^{+2} ratio of two was established using $Fe_2(SO_4)_3$ as above. In this case the iodine tracer was distilled out at the rate of forty-seven minutes for a 50% yield. When 1 mg of carrier was added the time required for recovery of 50% of the iodine was four minutes.

Recommendations

Dissolution: Wrap uranium metal in platinum gauze. Dissolve in 2.2 liters of concentrated HCl per slug at the boiling point for one hour. At this time 90% of the metal should be dissolved. Since the I^{135} will have decayed to 90% of the initial activity the over all yield should be about 80%.

Oxidation: Add 100 ccs of saturated $Fe_2(SO_4)_3$ solution and 2 mgs of carrier iodine as iodide per slug to the dissolver solution. Then add a saturated $Li_2Cr_2O_7$ solution as rapidly as the violence of the reaction permits until the end point is approached. In the experimental work, 100 ccs of solution was required for a quarter slug of metal and this was added in twenty to thirty minutes. The $Li_2Cr_2O_7$ solution was added through a coarse

sintered glass filter below the surface of the UCl_4 solution. Add the $Li_2Cr_2O_7$ solution until the U^{+4} end point is reached as indicated by platinum and tungsten electrodes. With the tungsten electrode no EMF is shown until within a few per cent of the end point where the EMF reaches a maximum. When the end point is reached, add 200 ccs of saturated $Fe_2(SO_4)_3$ solution per slug.

Distillation: Because of the low iodine concentration and the high chloride ion concentration, the vapor pressure of iodine over the solution is very low relative to that of water. It is therefore necessary to use a fractionating column in order to reduce the amount of water distilled over. It is estimated that two theoretical plates, one in the still and one in the condenser, are sufficient. In the experimental work an unpacked twelve inch egg condenser was used. Cooling water was run in at the top at such a rate that about 95% of the water was condensed.

Use a $PdCl_2$ solution into which SO_2 is bubbled as a receiving solution for the iodine. Pass a slow current of air into the still to prevent back diffusion of SO_2. Reflux the solution as rapidly as possible without flooding the column. Control the temperature of the condenser so that not more than 15 to 20 ccs of water are distilled over in thirty minutes. Reflux for ten minutes, then add 2 mgs of iodine carrier per slug and continue refluxing until the rate of distillation is approximately equal to the rate of decay of I^{135}. At this point, shut off the SO_2 and remove the cooling water from the condenser. Aeration of the hot receiving solution will remove the SO_2 and allow precipitation of PdI_2.

Assuming that the oxidation and distillation are completed in one hour, a yield of 80% including decay should be expected for these steps. The over all yield of I^{135} including decay from the time solution of the metal is started should be between 60 to 65%.